ARMY RESEARCH LABORATORY

Functionally Graded Adhesives

by Christopher B. Stabler, Faye R. Toulan, and John J. La Scala

ARL-TR-5034 **November 2009**

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14. ABSTRACT
The goal of this project was to increase rubber to metal adhesion in Army materials using the concept of functionally graded interfaces as observed in squid beaks. Through application of adhesive as a graded interface with layers of varying rigidity, exceptional adhesion can be accomplished. 3M Scotch-Weld 847 was chosen as the adhesive because of its flexibility, potential for use on Army weapons platforms, and because it contains no hazardous air pollutants. Talc, silica, and calcium carbonate fillers at various loading levels were added to increase the rigidity of the adhesive. Various methods were employed to optimize the dispersion of the filler in the adhesive. Testing with 5, 10, and 12.5 lb loads, as well as, Instron instrumental testing illustrated that a graded interface at various percentages provides superior adhesion than a non-graded system or the neat baseline adhesive.

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1. Introduction/Background

A squid beak is among the hardest and stiffest wholly organic materials known (*1*). However, the rest on the creature is compliant. Yet, the squid is able to deliver very high crushing forces with its beak (*1*). Mechanically mismatched man-made materials lead to high interfacial stress and contact damage (*1*). Analysis of the squid has shown that the transition from the extremely stiff beak to the softer muscle mass is graded, such that the stiffness of the beak gradually decreases two orders of magnitude from the tip of the beak to the base of the beak (*1*). Figure 1 depicts this visible gradient.

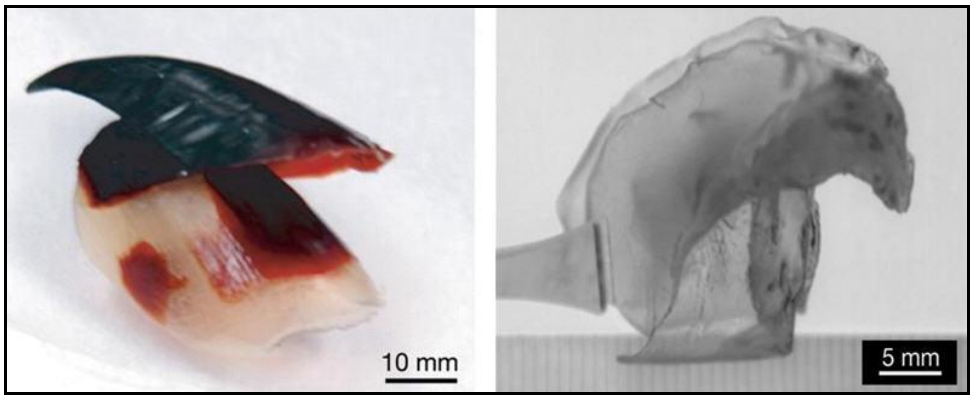

Figure 1. Beak of the Humboldt squid (left), Optical image of the Humboldt squid beak (right).

Literature has postulated that this graded idea can be used to improve the bonding of mechanically mismatched materials. Rubber and metal are mechanically mismatched and often used together by the Department of Defense (DoD) and commercial industry. Some examples of rubber to metal bonding by the DoD include treads and road wheels for tanks, composite armor concepts, submarine damping and underwater electrical connectors, and rubber sealant material that is ubiquitous.

Common adhesive application for rubber to metal bonding utilizes spray or brush methods (*2*). Adhesive is applied to each substrate and cured at room temperature for a varying amount of time depending on the formulation (*2*). Next, the coated rubber and metal substrates are adhered (*2*). Thermoset adhesives are applied to unvulcanized rubber and require heat and compression to create the bond (*3*). Cold set adhesives are applied to vulcanized rubber and do not require heat to create the bond (*3*). Application of adhesive is more effective when applied to both substrates, and multiple coats may be required if a porous substrate is implemented (*4*).

It is a known concept that nanoparticles and microparticles can be used to increase the rigidity of polymeric materials (*5*). In fact, most commercially available adhesives contain a significant level of fillers to help increase viscosity, provide pigment, increase volume, lower cost, modify

strength, and alter adhesive properties (*3*). Calcium carbonate and talc are inexpensive commonly used fillers (*6*). Titanium dioxide is used to add pigment to an adhesive (*7*). Fumed silica is employed as a rheology modifier (*8*).

The goal of this work is to determine whether an adhesive with a stiffness gradient from the metal to the rubber interface can improve rubber to metal bonding. For simplicity, we have chosen to examine adhesives/substrates conforming to military specification MMM-A-121, which applies to secondary bonding of vulcanized rubber to metal (*2*). Specifically, this work examines the addition of various nanoparticles and microparticles to a commercial product to construct this graded adhesive. By adding nanoparticle and microparticle fillers to a compliant adhesive and forming a graded structure in which a multilayer bond is formed with increasing rigidity toward the metal, the strength of a bond may be significantly enhanced. Because MMM-A-121 adhesives are applied in three coats, the concept is to apply the first coat of adhesive to the rubber without the addition of nano/microparticles. The second coat applied to the rubber will contain an intermediate amount of nano/microparicles. The coat applied to the metal will contain a high content of nano/microparticles. This functionally graded system can include a greater number of filled adhesive layers. Although this research applies to studies involving three coats of adhesive, a system involving far more coats to gradually change the rigidity across the adhesive application could be evaluated. This report examines the effect of the graded adhesive design to the baseline (neat) adhesive and non-graded filled adhesive systems to determine improved rubber to metal bonding.

2. Experimental Procedures and Calculations

2.1 Flexibility

An adhesive was chosen that had flexibility and modulus similar to that of typical rubbers so that the first layer of adhesive applied to the rubber would only result in a small stiffness change at the interface. There were three adhesives and sealants chosen for flexibility testing: 3M Scotch-Grip* Rubber and Gasket Adhesive 847 (3M-847), a hazardous air pollutant (HAP) free adhesive, OSI QUAD† Advanced Formula Sealant (Quad), a solvent based sealant, and DAP DYNAFLEX 230‡ Sealant (Dynaflex 230), a water based acrylic latex sealant. Using a 6.5 mil Byrd applicator to create a continuous film, the three products were applied to release paper. The films cured at room temperature for 1 day and then placed in an oven at 50 °C for varying durations ranging from 1 to 120 hours (h). Another sample was cured at room temperature for comparison to the accelerated heat aged samples. After the selected duration, the samples were removed from the oven and peeled off of the release paper. The samples were bent and stretched

* 3M is trademark of the 3M Company.

† OSI is a registered trademark and QUAD is a trademark of OSI Sealants, Inc.

‡ DAP and DYNAFLEX 230 are both registered trademarks of DAP Products Inc. and/or DAP Brands Company.

by hand to determine flexibility by qualitative observation. The 3M-847 was chosen to continue testing because of its extreme flexibility, prescribed use as a rubber to metal adhesive, and environmental friendliness (*4*).

2.2 Filler Dispersions in Solvent

Several particle fillers were dispersed in acetone. The fillers were mixed directly into the solvent to examine behavior in solution, such as their proclivity to disperse and duration of suspension. Additionally, in an effort to optimize the loaded filler weight percent without changing the adhesive viscosity, the filler would be "let down" (i.e., pre-wetted) with acetone before adding the adhesive. Acetone was chosen, because it is the primary solvent used in 3M-847 adhesive according to the Material Safety Data Sheet (MSDS) (*9*). The initial emphasis was to add as much filler to the acetone as possible in order to have the potential of rigidizing the adhesive to the highest extent. There were several fillers utilized for this study: Cab-o-sil M5 fumed silica, talc, calcium carbonate, and 3M Glass Bubbles K37. These fillers are commonly used in adhesive formulation (*10*). Varying amounts of filler were added to a vial. Acetone was then added to the vial. After capping, the vial was mixed. There were several mixing methods used to create adequate homogeneity. Hand mixing with a spatula, shaking the vial, placing the vial in a Thinky ARE-250 orbital mixer, and utilizing a Model 75D Aquasonic sonicator were the mixing methods utilized.

2.3 Adhesive Dispersions

As a result of the excellent performance of the Thinky ARE-250 orbital mixer for blending filler into solvent, this mixer was exclusively used for adhesive dispersions. The dispersions were prepared using two methods. In the first method selected samples were prepared by blending the adhesive and filler with no added solvent. In the second method, adhesive dispersions were prepared by initially blending filler/acetone then adding 3M-847. Talc, fumed silica, and calcium carbonate were selected as the fillers for the adhesive dispersions. Observations were made about the homogeneity of the mixture. Focus was set on adding as much filler to the adhesive dispersion as possible, while maintaining adequate homogeneity. The added weight percent filler to adhesive solids, F, added relative to the total solids content of the adhesive dispersion was derived from equation 1 for the total solids content:

$$\%solids_T = \frac{\%solids_A \times mass_A + \%solids_d \times mass_d}{mass_T}, \tag{1}$$

where the subscripts *T*, *A*, and *d* denote the total adhesive dispersion, adhesive, and filler/acetone dispersion, respectively. The F value was calculated from equation 2:

$$F = \frac{mass_f}{\%solids_A \times mass_A + mass_f}, \tag{2}$$

where the subscript *f* denotes the added filler content.

2.4 Aluminum Foil Testing

Before rubber and metal substrates were used for testing, aluminum foil was bonded together to qualitatively assess the adhesion of each of the adhesive dispersions. Fumed silica, talc, and calcium carbonate filled adhesives were tested. These dispersions were all tested when F was 1%, 5%, 10%, and 15%. Fumed silica trials were also completed for F equal to 25%, 34%, 42%, 52%, and 73%. Foil was cut into 6×1 inch strips. This test was used to determine the added filler loading threshold where the adhesion was negatively affected by the filler and to determine whether added filler at any level can improve adhesion strength. Release tape was placed on each foil piece to prevent foil tensile failure during experimentation; this tape would provide a clean edge to begin testing. A single coat of each adhesive dispersion was applied with a brush to both pieces of the aluminum foil. Only one type of adhesive dispersion was used per foil assembly. Each assembly consisted of two coats of adhesive dispersion, one on each aluminum foil substrate. The adhesion strength was given a subjective rating between 0 (weakest) and 12 (strongest).

2.5 Adhesive Dispersion Non-Graded Testing

Rubber substrates were neoprene, with dimensions 6 long×1 wide× 0.25 thick inches; while the unpolished steel substrates were 6 long×3 wide×0.032 thick inches conforming to the specifications of MMM-A-121 (*2*) (refer to figure 2). Using rubber and metal substrates, the adhesive dispersions filled with fumed silica, talc, or calcium carbonate were tested for adhesion strength. There were two coats of adhesive dispersion applied to the rubber substrate and one coat applied to the metal, for a total of three coats of adhesive per assembly. First, a baseline sample of neat adhesive was prepared using the 3M-847 adhesive with no added fillers for all three layers. Adhesive is applied to the rubber substrate and allowed to dry before a second coat is added. The adhesive is applied to an area of 4×1 inches on both substrates. The two substrates are then adhered when the adhesive is aggressively tacky and pressed with a roller. Non-graded filled adhesive samples were prepared in the same manner using the adhesive with the same filler content in all three layers. Adhesive formulations were prepared using talc (F=1, 5, 10, 15, and 30%), silica (F=1, 5, 10, and 15%), and calcium carbonate (F=1, 5, 10, and 15%) as fillers.

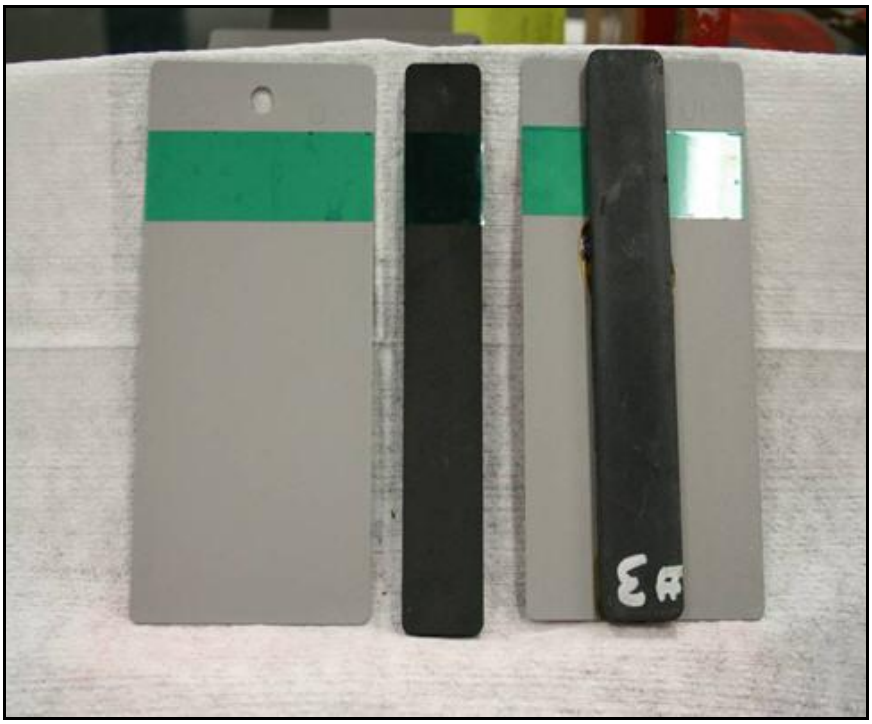

Figure 2. Steel and rubber substrates.

After the rubber to metal assemblies were conditioned at room temperature in the hood overnight, they were placed in the oven at 50 °C for 5 days. When the 5 days of accelerated heat aging at 50 °C was completed, the samples were cooled at room temperature for 30 min before testing. The samples were examined using a strip adhesion test in which weight is secured to the rubber and suspended at an angle of approximately 90°, with respect to the steel panel and the rubber assembly pulling on the adhered bond (*2*). The hardware and assembly is shown in figures 3 and 4. The samples were tested using a 5 pound (lb) weight according to the MMM-A-121 specification, as well as 10 and 12.5 lb weights to further stress the adhesive bond to failure (refer to figures 3 and 4). A 5 lb weight was attached and held by the sample for 3 min. If complete failure was not observed, a 10 lb weight was placed on the hook and tested for an additional 3 min. As before, if complete failure was not observed within the 3 min test interval, a 12.5 lb weight was placed on the hook and tested for an additional 3 min. After each analysis interval, the amount of rubber to metal delamination was measured.

Figure 3. Clamps, screws, and bolts for strip adhesion testing (left). Weights for testing (right).

Figure 4. Strip adhesion test of the 3M-847 adhesive (left). Testing setup (right).

2.6 Adhesive Dispersion Graded Testing

The purpose of this study was to determine if there was a significant difference between a graded and non-graded interface. The adhesive dispersions were used to create a graded system. By applying particle filled adhesive on the rubber and metal substrates, this graded interface was created. Two samples were created for each graded system; one assembly conditioned at room temperature, while the other would be placed in the oven at 50 °C. On the rubber substrate, neat 3M-847 (i.e., no added filler) was applied as the first coat. This adhesive was allowed to dry and a coat of low added filler adhesive dispersion was applied on top of the 3M-847 (neat). One coat

of higher added filler adhesive was applied to the metal substrate. The two substrates were bonded when the adhesive was still wet or aggressively tacky. These samples were pressed with a roller and conditioned at room temperature from 4 to 5 days. The samples were then placed in the oven at 50 °C for 5 days. The heat aged samples cooled at room temperature for 30 min before being tested. The room temperature samples were tested 5 or 6 days after they were created. A trial involving neat 3M-847 was also created for comparison. As for the non-graded case, the 5, 10, and 12.5 lb weights were all used.

2.7 Instron Testing

Based on previous 90° strip adhesion testing, several graded interfaces were tested on an Instron equipped for a 90° constant angle peel test. The samples tested included: 0/1/5% fumed silica, 0/1/5% talc, 0/5/10% talc, 0/1/5% calcium carbonate, and 0/5/10% calcium carbonate. The neat adhesive and all corresponding non-graded, filled systems were also tested. After the samples were prepared, they cured at room temperature for 4 days and then experienced accelerated curing at 50 °C for 2 days. Approximately 2 inches of un-bonded surface on the rubber to metal assembly was placed within the clamps on the Instron. Force was applied through the machine, and the peak loads of the samples were compared. Three samples per interface were tested.

3. Results and Discussion

3.1 Flexibility

The adhesive films were smooth, flexible and easily removed from the release paper (refer to figure 5). The 3M-847 had the least flexible and pliable film of the tested products; however, as an adhesive, a stiffer film is expected. The sample of 3M-847 that force cured in the oven for 120 h remained sufficiently flexible. The Quad and Dynaflex 230 sealants were easy to remove from the release paper, produced smooth films, and had excellent flexibility. However, these sealants were not prescribed for rubber to metal bonding. All of the tested films had an acceptable flexibility level. A high compliance is desired, as the rigidity of the adhesive can be increased through the addition of particle fillers. It would be more difficult to plasticize a rigid material through post production additions without sacrificing adhesion.

Figure 5. Dried films of 3M-847 (left), Quad (middle), and Dynaflex 230 (right).

3.2 Filler Dispersions in Solvent

This testing determined the amount of filler that could be added to pure acetone, as well as the miscibility of the fillers in the solvent. The fumed silica, suspending agent, was easily mixed into the acetone. The fumed silica, possessing a low density, occupies a large volume. As a result, at approximately 15% silica, the solution became a thick gelatinous mixture and no additional silica could be dispersed. Glass bubbles performed poorly when mixed with acetone at all tested percentages. These glass bubbles, which are commonly used to lower product density and product weight (*11*), resisted wetting by the solvent and immediately floated to the top of the liquid in the vial. Therefore, the glass bubbles were eliminated from future testing, as they would not maintain adequate miscibility in solution. The talc and calcium carbonate acted similarly to each other when dispersed in acetone. Both of the tested fillers were miscible when mixed; however, the suspension was not stable and the filler quickly settled out of solution. The talc dispersion remained mixed for a few minutes, while the calcium carbonate dispersion settled out of solution within a few seconds after mixing. A theoretical solids of 15% seemed optimum, as additional amounts were never fully mixed.

3.3 Adhesive Dispersions

The adhesive dispersions testing allowed for further analysis of the additional particle filled adhesive. Dispersions containing fumed silica were miscible in the adhesive and remained suspended over time. On the other hand, adhesive dispersions using talc or calcium carbonate were not stable and settled over time. As a result, it was necessary to re-mix these formulations prior to application.

The initial 5 min blending of the acetone and filler allowed for a successful dispersion before the adhesive was added. When the 3M-847 was added to the vial, quickly hand mixed, and then placed in the orbital mixer for an additional 5 min, the samples were homogeneous. This method

provided ten total minutes of blending without excessive heat generation common when the Thinky ARE-250 is used consistently for 10 min or more. Adhesives can be sensitive to heat and high temperatures resulting in negative effects on adhesion performance (*12*).

Over 70% added fumed silica was successfully blended with the adhesive when pre-dispersed in acetone. Fumed silica failed to successfully mix when adding the 3M-847 directly to the dry fumed silica. This dispersion, although only having an F value of 33%, became solid and possessed insufficient liquid (refer to figure 6). Using the acetone to let down the filler prior to adding to the adhesive, allows it to be added to the adhesive without significantly changing the viscosity. Even though focus was placed on loading the adhesive the maximum amount of filler, there was an addition threshold that significantly affected the adhesion. The 3M-847 was filled with talc to an added weight percent of 30%. Figure 6 illustrates a successfully miscible adhesive dispersion involving talc. Calcium carbonate, being the filler with the greatest proclivity to settle out of suspension, only had a capacity of 15% added filler. Due to the viscosity of 3M-847, the added filler remained miscible for a longer duration than when dispersed in just acetone. Additionally, more filler was able to be loaded into the adhesive than predicted previously, because the 3M-847 contains acetone that was utilized in mixing. Successful dispersions were created for fumed silica, talc, and calcium carbonate with F values of 1, 5, 10, and 15%. A 30% talc dispersion was also created. The total mixing time of 10 minutes (min) in the Thinky ARE-250 orbital mixer also yielded well blended samples.

Figure 6. Sample prepared by adding dry fumed silica to adhesive (left). Successfully blended adhesive dispersion (right).

3.4 Aluminum Foil Testing

Results of the aluminum foil adhesion testing are shown in table 1. These tests gave valuable insight as to the F_{max} for each filler. Silica samples having an F value above 50% had no adhesion to the aluminum foil substrates. There was too much fumed silica to be properly wetted by the adhesive at these high levels, resulting in an adhesive that crumbled between the substrates.

Results showed that force curing at 50 °C yielded stronger adhesion than samples that were kept at room temperature for the same duration. Additionally, the adhesive dispersions with added talc and calcium carbonate provided better adhesion than the neat 3M-847. In these talc and calcium carbonate trials, the aluminum foil exhibited substrate failure and would tear before the bond strength was affected. All samples tested exhibited a cohesive failure of the adhesive.

Table 1. Aluminum foil testing results using 0–12 adhesive strength scale.

Filler	Percent Added Filler, F (%)	Temperature	Strength Rating
Neat 3M-847	0	50 °C	10
Fumed Silica	1.06	50 °C	9
Fumed Silica	4.93	50 °C	9
Fumed Silica	9.96	50 °C	9
Fumed Silica	14.73	50 °C	6
Fumed Silica	25.50	50 °C	4
Fumed Silica	32.91	50 °C	4
Fumed Silica	34.21	50 °C	3
Fumed Silica	41.88	50 °C	2
Fumed Silica	51.56	50 °C	0
Fumed Silica	73.35	50 °C	0
Talc	0.99	50 °C	12
Talc	4.93	50 °C	12
Talc	9.81	50 °C	12
Talc	14.65	50 °C	12
Calcium Carbonate	1.00	50 °C	11
Calcium Carbonate	4.38	50 °C	11
Calcium Carbonate	9.22	50 °C	10
Calcium Carbonate	12.46	50 °C	10
Neat 3M-847	0	RT	9
Fumed Silica	1.06	RT	7
Fumed Silica	4.93	RT	8
Fumed Silica	9.96	RT	8
Fumed Silica	14.73	RT	6
Fumed Silica	25.50	RT	5
Fumed Silica	32.91	RT	4
Fumed Silica	34.21	RT	3
Fumed Silica	41.88	RT	2
Fumed Silica	51.56	RT	2
Fumed Silica	73.35	RT	0
Talc	0.99	RT	9

Table 1. Aluminum foil testing results using 0–12 adhesive strength scale (continued).

Filler	Percent Added Filler, F (%)	Temperature	Strength Rating
Talc	4.93	RT	8
Talc	9.81	RT	9
Talc	14.65	RT	8
Calcium Carbonate	1.00	RT	9
Calcium Carbonate	4.38	RT	8
Calcium Carbonate	9.22	RT	8
Calcium Carbonate	12.46	RT	7

3.5 Adhesive Dispersion Non-Graded Testing

This testing was completed to examine the strength of the adhesive dispersions in a non-graded interface. Because 3M-847 is a finished product with an expectedly optimized formulation, addition of filler was not expected to improve the adhesion strength. Nevertheless, the tested samples preformed very well, in most cases outperforming the neat adhesive (refer to table 2 and figure 7). The fumed silica adhesive dispersions yielded the strongest adhesion, and the dispersions with an F value of 10 and 15% were the only samples to hold 12.5 lb for 3 min. All other samples, including the neat 3M-847 failed at 10 lb within 3 min, where the total 4 inch bonded area is delaminated. There were unexpected failures for this non-graded testing; 5% talc, 15% talc, and 15% calcium carbonate all yielded complete failure within 3 min of testing at 5 lb. This data is unexpected because samples with larger F values did not fail. The reason for this failure is unknown and will be further analyzed.

Table 2. Bond remaining in non-graded interface after testing with 5, 10, and 12.5 lb.

Filler	Percent Added Filler, F (%)	Bond Remaining after 5 lb (in)	Bond Remaining after 10 lb (in)	Bond Remaining after 12.5 lb (in)
Neat 3M-847	0	2.88	Failure	Failure
Fumed Silica	0.965	3.97	Failure	Failure
Fumed Silica	4.55	3.56	Failure	Failure
Fumed Silica	9.26	4.00	3.88	3.50
Fumed Silica	13.3	4.00	3.88	3.38
Talc	0.897	0.75	Failure	Failure
Talc	4.52	0.00	Failure	Failure
Talc	9.2	3.88	Failure	Failure
Talc	13.64	0.00	Failure	Failure
Talc	30.12	3.69	Failure	Failure
Calcium Carbonate	0.905	2.50	Failure	Failure
Calcium Carbonate	4.38	3.75	Failure	Failure
Calcium Carbonate	8.79	0.00	Failure	Failure
Calcium Carbonate	13.66	3.81	Failure	Failure

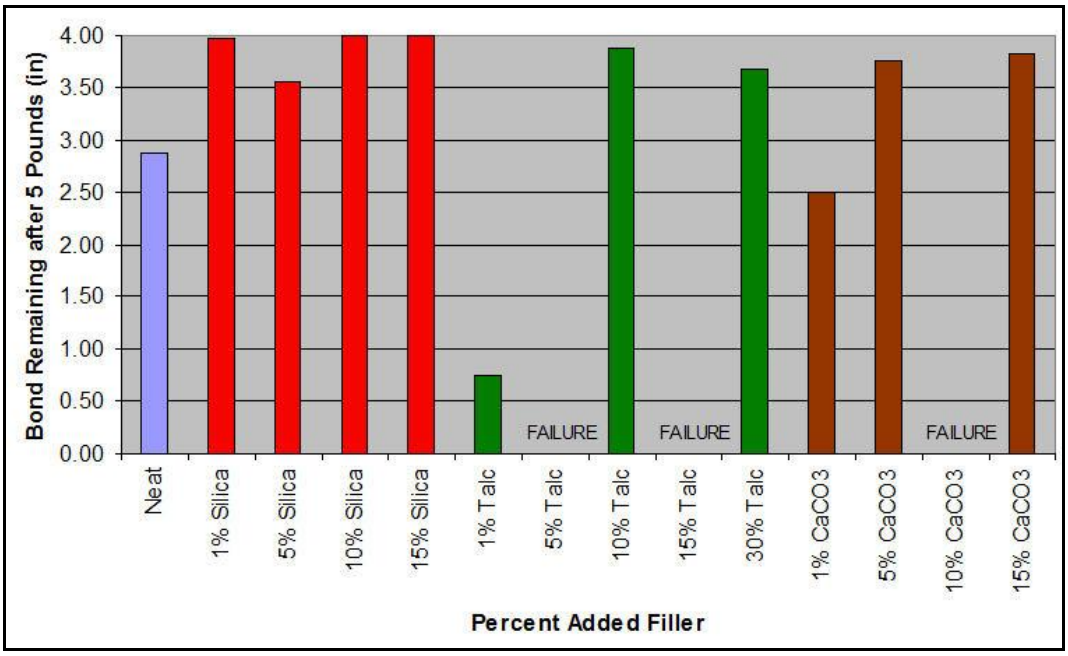

Figure 7. Bond remaining after testing with 5 lb for a non-graded interface.

3.6 Adhesive Dispersions Graded Testing

Although some adhesive dispersions performed poorly in the non-graded system, they were still investigated in the graded testing. The postulated strength increase in a graded system is not correlated to the strength of the individually filled adhesive dispersions. Several tested graded interfaces provided superior adhesion compared to the baseline 3M-847. No specific filler or percentage gradient was significantly better than another, with promising results observed at various F values. Analysis with 12.5 lb demonstrated that the graded interfaces utilizing 1/5% fumed silica, 5/15% talc, and 5/15% calcium carbonate provided the strongest adhesion. Results, shown in table 3, are similar to those exhibited by figure 8. These results clearly showed that some graded formulations perform not only better than the neat adhesive, but also out-perform the non-graded filled adhesive systems.

Table 3. Bond remaining in functionally graded interface after strip adhesion testing with 5, 10, and 12.5 lb.

Filler	Percent Added Filler (F), Rubber Coat (%)	Percent Added Filler (F), Metal Coat (%)	Bond Remaining after 5 lb (in)	Bond Remaining after 10 lb (in)	Bond Remaining after 12.5 lb (in)
None	0	0	4.00	3.94	Failure
Talc	0.897	4.52	4.00	3.97	Failure
Talc	4.52	9.2	4.00	3.75	Failure
Talc	9.2	13.64	4.00	3.81	Failure
Talc	4.52	13.64	4.00	3.56	3.13
Fumed Silica	0.965	4.55	4.00	3.81	3.25
Calcium Carbonate	4.38	13.66	4.00	3.88	3.25

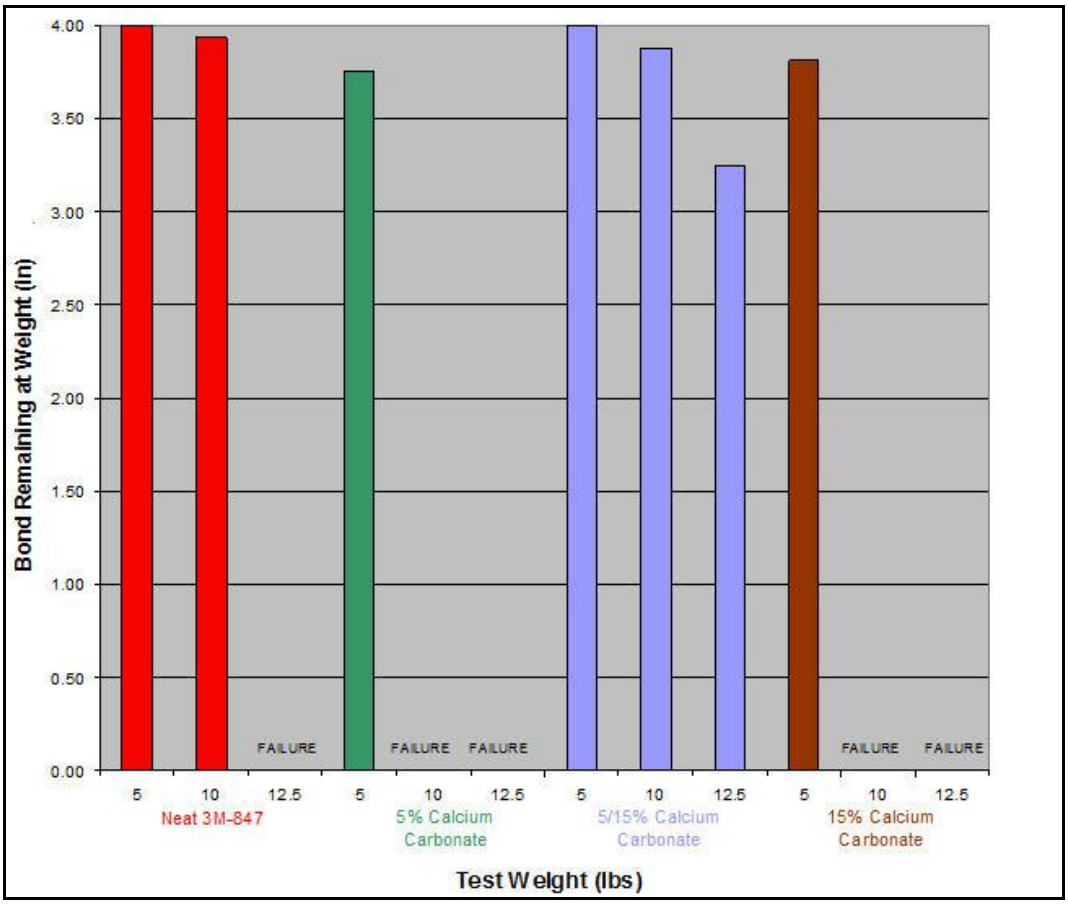

Figure 8. Bond remaining after strip adhesion testing.

3.7 Instron Testing

Figure 9 shows several of the graded assemblies outperformed the control 3M-847: 0/1/5% talc and 0/1/5% fumed silica gave the strongest bond. Several of the graded assemblies outperformed the control 3M-847: 0/1/5% talc and 0/1/5% fumed silica gave the strongest bond. These samples had an average peak load around 11 lbf. The most successful samples were non-graded and filled; at low F values for talc, fumed silica, and calcium carbonate, strength was paramount. All of the tested assemblies exhibited adhesive failure, with all the adhesive remaining on the steel substrate.

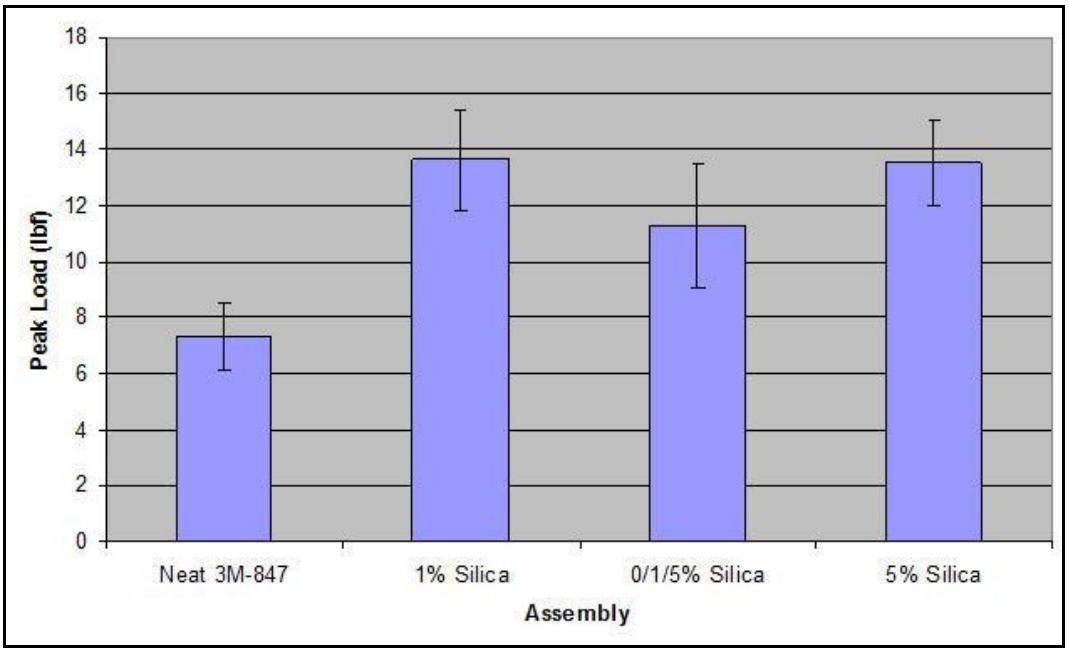

Figure 9. Peak load values for the control, non-graded, and graded interfaces containing fumed silica.

The graded interfaces commonly provided superior adhesion compared to the non-graded baseline 3M-847. However, there were instances where the graded system did not optimize adhesion; further examination must be completed to determine why certain percentage couplings generate stronger adhesion than other formulations.

4. Summary and Conclusions

Application of rubber to metal adhesives in a functionally graded interface can provide superior adhesion relative to a non-graded system or non-filled system. Adhesion was stronger for many of the graded interfaces, with the 0/1/5% talc, 0/1/5% fumed silica, and 0/1/5% calcium carbonate systems yielding the strongest bond in the three coat structure. As a three coat interface, there was excellent adhesion. However, it is postulated that the application of more coats would result in a more finely graded interface more analogous to the squid beak (*1*). There is much work that can be completed to categorize and further analyze this graded system to provide more reproducible data. Additional testing needs to be completed on multilayer interfaces and the use of multiple fillers in the same system. Lastly, examining the morphology and other physical properties of the successful vs. un-successful graded systems must be performed to better understand and formulate these adhesives.

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